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**SELECTION OF ANALYTICAL PROCEDURES FOR DETERMINING THE RESIDUAL
SULFIDE LEVELS FOLLOWING BLACK LIQUOR OXIDATION**

Project 2963

Report One

A Progress Report

to

**NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR
AIR AND STREAM IMPROVEMENT, INC.**

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THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

SELECTION OF ANALYTICAL PROCEDURES FOR DETERMINING THE RESIDUAL
SULFIDE LEVELS FOLLOWING BLACK LIQUOR OXIDATION

SUMMARY

The purpose of this project is to establish useful quantitative procedures for the determination of inorganic sulfide and, if possible, organic sulfides in oxidized black liquor (OBL). The sulfide concentration range must be from 0.0 to 0.5 g./l.

The use of a sulfide antioxidant buffer (SAOB) made it possible to sample, store, and handle OBL samples for reasonable time periods without further oxidation occurring. Modifications of potentiometric and colorimetric methods available were studied because of their convenience and sensitivity. Two alternate procedures are recommended. Each begins with the isolation of volatile sulfides by a gas sweep method, and each is effective in different but complementing concentration ranges.

The OBL in SAOB is mixed with potassium hydrogen phthalate buffer and the volatile sulfides are transported by means of nitrogen gas sweep into a sulfide absorbing solution. For inorganic sulfide concentrations of 10^{-1} to 10^{-4} M (about 3.0 to 0.003 g./l.) SAOB can be used as the scrub. The sulfide is then determined by potentiometric titration using a sulfide specific ion electrode with a double junction reference electrode and $\text{Cd}(\text{NO}_3)_2$ as titrant. For inorganic sulfide concentrations of 10^{-3} to 10^{-6} M (about 0.03 to 0.00003 g./l.) CdSO_4 -boric acid, 1 and 2% by weight, respectively, is used as the scrub. The sulfide is then determined colorimetrically from the methylene blue produced from the sulfide.

These methods with appropriate corrections gave results within $\pm 5\%$ of the known values for Na_2S solutions. They gave similar accuracy in the analysis of OBL

samples to which a known amount of Na_2S was added. They require an elapsed time of about one hour and may be set up and carried out by personnel with usual potentiometric skills.

Potentiometric titration of OBL samples directly in SAOB is possible with the above electrodes and titrant. However, the values were 1/3 to 1/5 of those found by the sulfide isolation procedure.

Direct potentiometry of OBL in SAOB was not useful. However, rough estimates of the sulfide absorbed in SAOB in the gas sweep procedure could be made by this method.

The determination of organic sulfides in OBL was attempted through isolation by the gas sweep procedure followed by selective absorption either in cold ($-78^\circ\text{C}.$) ethyl benzene, or in dilute AgNO_3 . Only marginal efficiency was obtained in either trap and the accuracy suffered from the diluteness of the AgNO_3 (10^{-4}M) required for the low sulfide contents. However, the sulfide isolation method coupled with selective absorbers and a coulometric titrator, or with a gas chromatograph should have the necessary selectivity and sensitivity.

INTRODUCTION

This is the final report on Project 2963 entitled "Selection of Analytical Procedures for Determining the Residual Sulfide Levels Following Black Liquor Oxidation." The object of this method evaluation is a definition of the specificity, sensitivity, and reproducibility of existing analytical techniques which are suitable for routine use by mill technicians. The suggested range of this investigation extends from 0.0 to 0.5 gram Na_2S per liter. Consideration was also given to the measurement of organic sulfides present.

The methods considered practical for oxidized black liquor (OBL) were potentiometric using the sulfide or the cadmium specific ion electrode for both inorganic and organic sulfides and isolation - colorimetric for inorganic sulfide. It will be shown that the latter method proved to be effective down to a minimum concentration in the OBL approaching 0.0001 g. Na_2S /liter ($\sim 1 \times 10^{-6}$ molar). Likewise, good potentiometric titrations of the inorganic sulfide in OBL can be obtained when the H_2S is isolated from the sample as in the colorimetric method. Finally, the organic sulfides cannot be handled by either of these approaches, but some practical solutions are indicated.

RECOMMENDED PROCEDURES

The steps followed are:

- (1) Place sample in stabilizing buffer
- (2) Acidify aliquot and sweep H_2S into trapping solution
- (3) Analyze trapping solution for sulfide content
 - (a) For concentrations from 10^{-4} to 10^{-1} molar sulfide use stabilizing buffer for trapping solution and analyze by potentiometric titration using a sulfide specific ion electrode and $\text{Cd}(\text{NO}_3)_2$ as titrant.
 - (b) For concentrations from 10^{-6} to 10^{-3} molar use a CdSO_4 -boric acid trapping solution, develop the methylene blue color, and analyze by absorbance measurements.

PREPARATION OF SAMPLE

Draw a quantity of the material to be tested and immediately place it in an equal volume of sulfide antioxidant buffer (SAOB) (1) in a glass container. The SAOB allows stable storage of a wide variety of sulfide solutions in a closed container for several weeks and in an open beaker long enough for normal laboratory handling.

THE RELEASE AND SCRUB OF HYDROGEN SULFIDE

Place a 10 ml. aliquot of the sample in a 500 ml. two or three neck (ground glass fitting) round bottom flask fitted with a nitrogen flushing line, a nitrogen bubbling line (a glass tube drawn to a capillary), and a liquid dropping funnel in one or two of the openings, and with a water cooled condenser in the remaining opening. See Fig. 1. The condenser should be straight walled and it should be held in the vertical position in order to minimize the amount of condensed water held on the inner

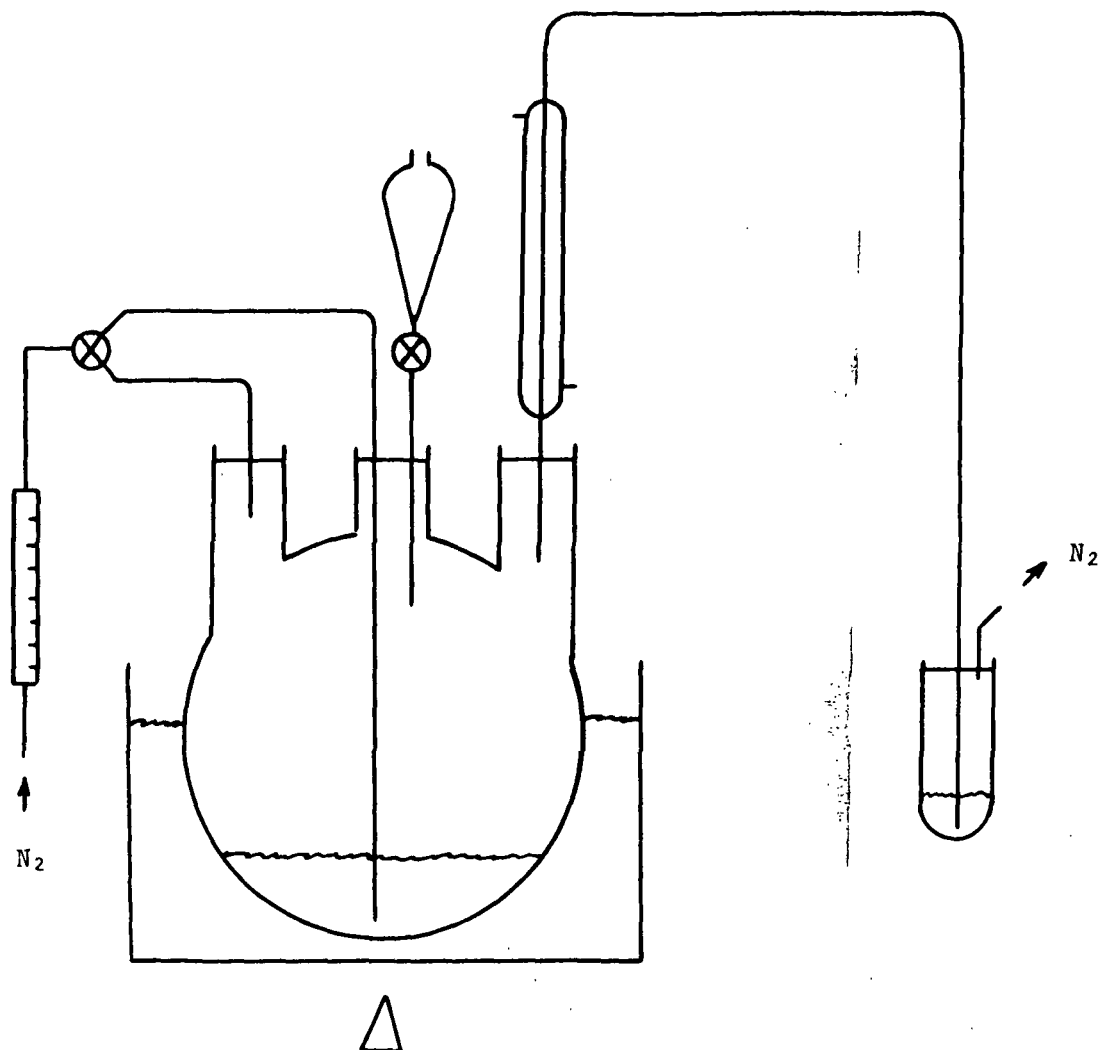


Figure 1. Schematic Diagram of the Gas Sweep Apparatus.

surface. An all glass line (joints may be made with shrinkable Teflon tubing) should lead from the condenser into the scrubbing tube, a 150 mm. x 25 mm. test tube, and it should taper to a capillary to serve as a bubbler. All connections should be glass to minimize H_2S sorption. Place 10.0 ml. of scrubbing solution (discussed below) in the trap and secure it to the bubbling tube. Nitrogen (O_2 free grade) is now passed through the system at the rate of about 100 ml./min. for about five minutes to flush out the air. Next add 90 ml. of 0.5 molar potassium hydrogen

phthalate (analytical reagent grade) to the flask by means of the dropping funnel. Immerse the flask in a boiling water bath. Switch the nitrogen flow to the bubbler tube and continue to bubble at about 20 ml./ min. for 30 min.

For very dilute samples requiring upgrading in concentration in the trap solution, use a one-liter flask, 100-ml. sample aliquot, 900 ml. of 0.5 molar potassium hydrogen phthalate, and maintain the bubbling in the flask for about 90 min. after originally flushing the air from the system. The volume of the scrubbing solution and all other steps in the procedure remain unchanged.

THE TRAPPING SOLUTIONS AND SULFIDE ANALYSIS

Potentiometric Titration: 10^{-4} to 10^{-1} Molar Sulfide

Place 10.0 ml. of SAOB (undiluted) in the trap as the scrubbing solution. After the run, carefully transfer this to a 50-ml. beaker. Rinse the scrubbing tube and bubbler with portions of 10.0 ml. of distilled water adding all of the rinse to the beaker. The beaker should finally contain the trapped H_2S in SAOB diluted 1:1 with a total volume of 20.0 ml., which is about the minimum volume that can be used in order to assure immersion of stirrer and electrodes. If any further dilution is necessary it should be done with SAOB diluted 1:1.

Place a Teflon coated magnetic stirring bar in the beaker and place this on a thin sponge on the stirrer platform so that the heat from the stirrer will not increase the temperature of the beaker. Immerse the tips of a sulfide specific ion electrode (Orion Model 94-16A, Orion Research, Inc., Cambridge, Mass.) and a double junction reference electrode (Orion, Model 90-02-00) in the sample. The outer solution of the double junction electrode should be 10% KNO_3 in 1.0 molar sodium hydroxide in order to match the pH of the SAOB diluted 1:1.

Titrate potentiometrically with an appropriate concentration of $\text{Cd}(\text{NO}_3)_2$ which was standardized with EDTA using Eriochrome black T as an indicator. Be sure to allow the system to come to equilibrium after each addition of titrant. This usually requires about one min. to as much as 5 to 10 min. as the end point is approached. The lower the concentration, the longer the time to come to equilibrium. Concentrations of standard $\text{Cd}(\text{NO}_3)_2$ as low as 10^{-3} molar may be stored and handled indefinitely without deterioration. Therefore, for sulfide concentrations approaching 10^{-4} molar, use a 100 ml. aliquot of the original sample in order to achieve about a tenfold increase in concentration in the trap.

The end point may be estimated from a plot of the measured EMF vs. the volume of titrant added. Or, a more accurate determination of the end point may be obtained from a Gran's plot (2), of the data. [This is a plot of $(\underline{V}_0 + \underline{V})10^{-\underline{E}/\underline{S}}$ vs. \underline{V} , where \underline{V}_0 and \underline{V} are the sample volume and titrant volume, respectively, \underline{E} is the measured EMF in millivolts, and \underline{S} is the slope of the Nernst equation, which is 30 millivolts for the sulfide ion at 25°C.] Divide the determined value by 0.85 to obtain sulfide content of the samples, as the recovering efficiency is about 85%.

Suggestion: for an original sulfide sample of unknown concentration, it may be desirable to dilute the scrub sample to 50 ml. and titrate a 25-ml. aliquot of this, say with 10^{-3} molar $\text{Cd}(\text{NO}_3)_2$ for an estimation of the sulfide content. The remaining 25-ml. aliquot may then be titrated with the most appropriate $\text{Cd}(\text{NO}_3)_2$ concentration. The initial EMF also will give a rough estimate of the sulfide content.

Colorimetric Determination by Methylene Blue Production:

10^{-6} to 10^{-3} Molar Sulfide

Place 10.0 ml. of a CdSO_4 -boric acid solution 1 and 2% by weight, respectively, in the trap as the scrubbing solution. Following a modified form of the method of Bamesberger and Adams (3), add 3.0 ml. of amine solution and one drop of ferric chloride solution to the contents in the trap. Be sure all of the CdS precipitate adhering to the glass wall and bubbler tube is dissolved. [This will assure accuracy for this sample and no carryover to the next sample.] Carefully transfer the clear trap solution to a 50-ml. volumetric flask. Use distilled water to rinse the bubbler and trap into the flask and fill to the mark. Mix the flask contents and allow to stand at room temperature for 30 min. before determining color. The color is stable for up to 3 or 4 hours, unless more than one drop of ferric chloride has been used by mistake. Measure the absorbance at 670 nm. and determine the sulfide concentration from a standard curve.

If the absorbance is greater than about 1.0 (sulfide concentrations greater than about 2.7×10^{-4} molar), a reasonable estimate of the sulfide concentration may be made by diluting an aliquot of the color with a solution containing CdSO_4 -boric acid at 0.2 and 0.4% by weight, respectively, in 0.55 molar sulfuric acid (3 parts acid to 97 parts water by volume). Divide the measured absorbance of the diluted color by 0.8 and determine the sulfide concentration from the standard curve using this corrected absorbance and the appropriate dilution employed. Our experience has indicated that dilution of the color as described results in an absorbance which is about 80% of the value expected from Beer's Law.

For samples with sulfide concentration approaching 10^{-6} molar, a 100-ml. aliquot of the original sample must be used in order to gain a tenfold increase in concentration in the trap.

The standard curve is obtained by running 10.0-ml. aliquots of sodium sulfide solutions of 0.5, 1.0, 2.0, and 3.0×10^{-4} molar in SAOB diluted 1:1 through the procedure and determining the absorbance. The sodium sulfide solutions are made by the appropriate dilution with SAOB (1:1) of a 10^{-1} molar Na_2S solution. This solution is prepared by placing 2.40 g. of washed and dried crystals of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ in a 100-ml. volumetric flask, adding 50 ml. of SAOB, and filling to the mark with distilled water. The precise concentration is determined by potentiometric titration with $\text{Cd}(\text{NO}_3)_2$.

RESULTS AND DISCUSSION

INORGANIC SULFIDE

Colorimetric Method

Modifications of the gas sweep method of Collins (4) to isolate and concentrate the volatile sulfides from OBL and the methylene blue color method of Bamesberger and Adams (3) were combined for the colorimetric method. A pH of 4 in the sparging solution is required in order to release the H_2S with only a minimum of SO_2 release. It was found that the 10% ammonium chloride solution suggested by Collins (4) was able to lower the pH of OBL or SAOB to only 7 or 8 which gave very low release of H_2S from samples with low ($<10^{-3}M$) sulfide concentration. The use of potassium hydrogen phthalate buffer kept the pH in the range of 4 to 5 and led to release of H_2S .

Listed in Table I are the known Na_2S concentrations and the measured absorbance. The data sets I-III from the original method were used to prepare the calibration curves presented in Fig. 2. Note that duplication and reproducibility are within +1%. It is also seen that $Cd(OH)_2$ suspension and $CdSO_4$ -boric acid systems lead to significantly different working curves. Thus, analysis of unknowns must be based on the appropriate working curve.

The $Cd(OH)_2$ suspension will trap H_2S and all other acid sulfides, such as mercaptans; however, the methylene blue color development is essentially from the inorganic sulfide only (5,6). Listed in Table II are the results of testing Na_2S solutions and OBL samples. The precision for most samples is within +5%. In view of the high precision and linearity of the working curves, the low accuracy of the Na_2S solutions is puzzling. This will be considered in later discussions.

TABLE I

METHYLENE BLUE CALIBRATION CURVE^a

Cd(OH) ₂			CdSO ₄ (1%) - Boric Acid (2%)			
I		II		III		IV
Na ₂ S Concn., M	Absorbance	Na ₂ S Concn., M	Absorbance	Na ₂ S Concn., M	Absorbance	Na ₂ S Concn., M
2.26 x 10 ⁻⁴	0.682	5.00 x 10 ⁻⁴	1.40 1.40	4.07 x 10 ⁻⁴	1.00	2.73 x 10 ⁻⁴
0.938 x 10 ⁻⁴	0.319	3.00 x 10 ⁻⁴	0.97 0.97	3.26 x 10 ⁻⁴	0.76	1.81 x 10 ⁻⁴
0.627 x 10 ⁻⁴	0.222	1.50 x 10 ⁻⁴	0.510 0.528	1.63 x 10 ⁻⁴	0.49	0.91 x 10 ⁻⁴
0.313 x 10 ⁻⁴	0.090	1.00 x 10 ⁻⁴	0.340 0.338	0.814 x 10 ⁻⁴	0.23	0.47 x 10 ⁻⁴
		0.50 x 10 ⁻⁴	0.13			

^aI, II, and III employed the original 0.25M potassium hydrogen phthalate buffer and gas train; and IV employed the improved H₂S release method and gas train.

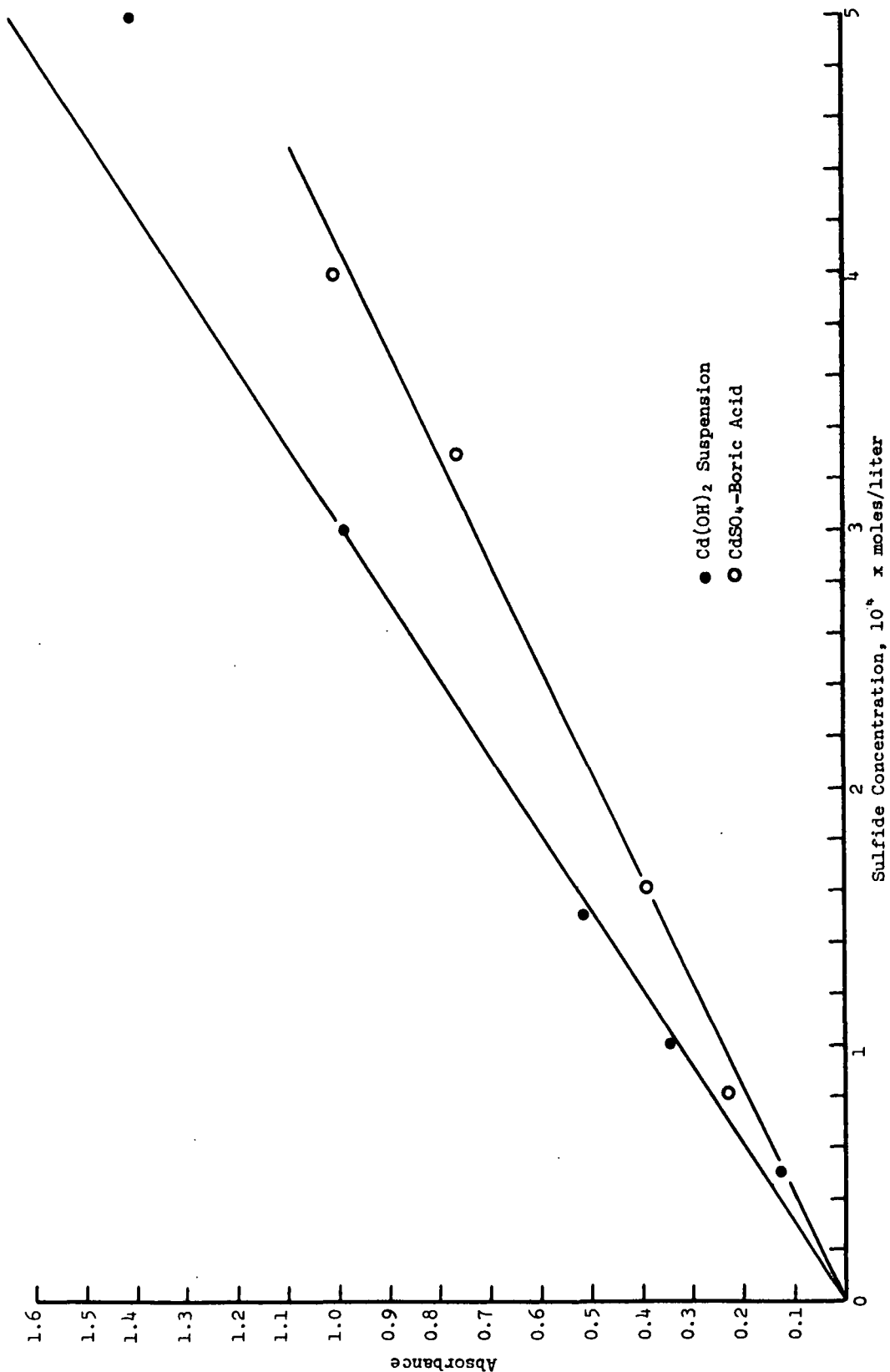


Figure 2. Calibration Curve for Sulfide Analysis by the Methylene Blue Original Method: Na_2S in SAOB Diluted 1:1 with Absorbance Measured at 670 nm.

TABLE II

SULFIDE ANALYSIS BY METHYLENE BLUE ORIGINAL METHOD
USING $\text{Ca}(\text{OH})_2$ SUSPENSION AS THE SCRUBBING SOLUTION

Sample	Sweep Gas	Absorbance at 670 nm.	Sulfide Conc., <u>M</u>
$0.82 \times 10^{-4} \text{M Na}_2\text{S}^a$	N_2	0.26	0.79×10^{-4}
		0.32	0.97
$0.82 \times 10^{-4} \text{M Na}_2\text{S}^a$	N_2	0.34	1.03
		0.34	1.03
		0.40	1.21
	Air	0.39	1.18
		0.39	1.18
	N_2	0.38	1.15
OBL-A		0.34	1.04
OBL-B	N_2	0.15	0.46
	Air	0.07	0.22
		0.09	0.28
OBL-C	N_2	0.262^b	1.60
		0.515	1.56
	Air	0.165^b	1.00
		0.310	0.94
OBL-F	N_2	0.132	0.405
		0.168	0.510

^aConcentration determined by potentiometric titration with standard $\text{Cd}(\text{NO}_3)_2$.

^bThe original sample size was 5.0 ml. instead of the usual 10.0 ml.

Since the $\text{Cd}(\text{OH})_2$ suspension was originally developed for absorbing H_2S from air samples, air was used as a sparging gas. [When air is used, the scrubbing solution must contain STRactan AF-2 (Stein-Hall and Co., Inc., distributors) in the amount of 1% as an antioxidant (3).] See Table II. On comparing the N_2 results with the air results it is seen that essentially 100% recovery was obtained when using Na_2S solutions, but only 50 to 60% recovery was obtained with the OBL. Air may thus be usable as a sparging gas if account is made for the lower recovery. Unless otherwise stated, nitrogen was used in the analyses given in this work.

Returning to the question of accuracy of sulfide recovery, Table III lists the results of adding known amounts of Na_2S to OBL samples. In the case of OBL-D recovery is 102% of the original plus added sulfide and in the case of OBL-E it is 110%. It therefore seems reasonable that the sulfide values determined by the methylene blue method are correct to within about $\pm 5\%$.

The data listed in Table III also show that a CdSO_4 -boric acid buffer (7) as scrubbing solution gives results equivalent to those obtained with $\text{Cd}(\text{OH})_2$ suspension. The CdSO_4 -boric acid solution has a pH of about 8 which will implement H_2S absorption but will allow the mercaptans and other organic sulfides to pass through for subsequent analyses. This equivalence of scrubbing solutions also suggests that mercaptans do not interfere with methylene blue color development in $\text{Cd}(\text{OH})_2$ system.

Listed in Table IV are the results of diluting a sample tenfold and recovering all of the sulfide content in the scrubbing solution. This results in a tenfold concentration increase in the isolation step by the gas sweep procedure. In the case of OBL-G there was 101% recovery which is perhaps fortuitous as the

TABLE III

THE DETERMINATION OF SULFIDE WITH KNOWN ADDITION TO OBL SAMPLES
USING THE METHYLENE BLUE ORIGINAL METHOD
WITH DIFFERENT SCRUBBING SOLUTIONS

Sample	Cd(OH) ₂	CdSO ₄ -Boric Acid	Percent Recovery
OBL-D	$0.57 \times 10^{-4} \text{M S}^-$		
OBL-D plus $0.752 \times 10^{-4} \text{M Na}_2\text{S}$	$1.34 \times 10^{-4} \text{M S}^-$		102
OBL-E		$0.70 \times 10^{-4} \text{M S}^-$	
OBL-E plus $0.814 \times 10^{-4} \text{M Na}_2\text{S}$		$1.66 \times 10^{-4} \text{M S}^-$	110

TABLE IV

DETERMINATION OF SULFIDE USING THE ISOLATION STEP
AS A MEANS OF CONCENTRATION VERY DILUTE SULFIDE SOLUTIONS

Sample	Sample Vol., ml.	Scrub Vol., ml.	Sulfide Conc., <u>M</u>	Recovery, %
OBL-G	10	10^b	4.56×10^{-4}	
OBL-G diluted ^a tenfold	100	10^b	4.59×10^{-4}	101
$8.14 \times 10^{-5} \text{M Na}_2\text{S}$ diluted ^a tenfold	100	10^c	7.30×10^{-5}	90
$9.14 \times 10^{-5} \text{M Na}_2\text{S}$	100	10^d	7.46×10^{-4}	82

^aThe dilution was made with equal volumes of SAOB and water.

^bCd(OH)₂ suspension, methylene blue analysis, original method.

^cCdSO₄-boric acid, methylene blue analysis, original method.

^dSAOB, potentiometric titration, improved method.

absorbance of these samples (1.50) is in the low accuracy range. The recovery of the Na_2S sample was 90% which is reasonably acceptable. The Na_2S recovery as measured potentiometrically is also reasonable as discussed later.

The limit of sensitivity at about $\pm 5\%$ level of accuracy would be the sulfide content of a 100-ml. sample concentrated tenfold in the scrubbing solution resulting in an absorbance of about 0.1. Based on the working curve this is a sample concentration of about $0.3 \times 10^{-5} \text{M S}^-$ (0.0001 g./l.). Absorbance measurements less than 0.1 are valid with increased error limits. At an absorbance of 0.02 the concentration limit would be about $0.06 \times 10^{-5} \text{M S}^-$ (0.00002 g./l.) with error limits of about $\pm 25\%$.

Potentiometric Methods

Sulfide Specific Ion Electrode

Potentiometric Titration. In light of the sensitivity and simplicity of sulfide specific ion electrode for sulfide analysis, as indicated in the work of Swartz and Light (8), potentiometric titrations were carried out on Na_2S solutions and on OBL. The titrant used was $\text{Cd}(\text{NO}_3)_2$ (1) (standardized with EDTA) thus avoiding the problem of reduction suffered when using AgNO_3 titrants for OBL (1,6).

To facilitate end point determination, all of the potentiometric titration data were analyzed according to a rectified form of the Nernst equation, the Gran's equation [see, for example, (2)]

$$(V_o + V)10^{-E/S} = 10^{-(E_o + E_j)/S} \gamma (C_o V_o - CV) \quad (1)$$

where \underline{V}_0 = initial volume of the unknown
 \underline{C}_0 = initial concentration of the unknown
 \underline{V} = volume of titrant added
 \underline{C} = concentration of the titrant
 \underline{E} = measured EMF
 \underline{E}_0 = standard EMF
 \underline{E}_j = junction EMF's
 $\underline{S} = \frac{2.303 RT}{nF}$
 \underline{R} = gas constant
 \underline{T} = temperature
 \underline{n} = valence of the specific ion under test
 \underline{F} = the faraday
 γ = activity coefficient of the specific ion.

Under constant conditions of pH and ionic strength, and with only one ion species undergoing change, a plot of $(\underline{V}_0 + \underline{V})10^{-\underline{E}/\underline{S}}$ vs. \underline{V} is a linear function with the intercept equal to the equivalence volume, \underline{V}_e . Being a linear function, only a few points are needed to determine the end point without going through the end point where the electrodes are most sluggish. Presented in Fig. 3 are typical plots of EMF vs. \underline{V} and its Gran's plot.

The SAOB was developed to provide constant pH and high ionic strength for solutions prepared from a wide variety of black liquor (BL) and OBL. A sample of BL was oxidized by sparging air through it at room temperature. Samples were taken at selected time intervals and immediately diluted with equal volumes of SAOB and water to give 10% solutions of OBL. Aliquots of these were potentiometrically titrated

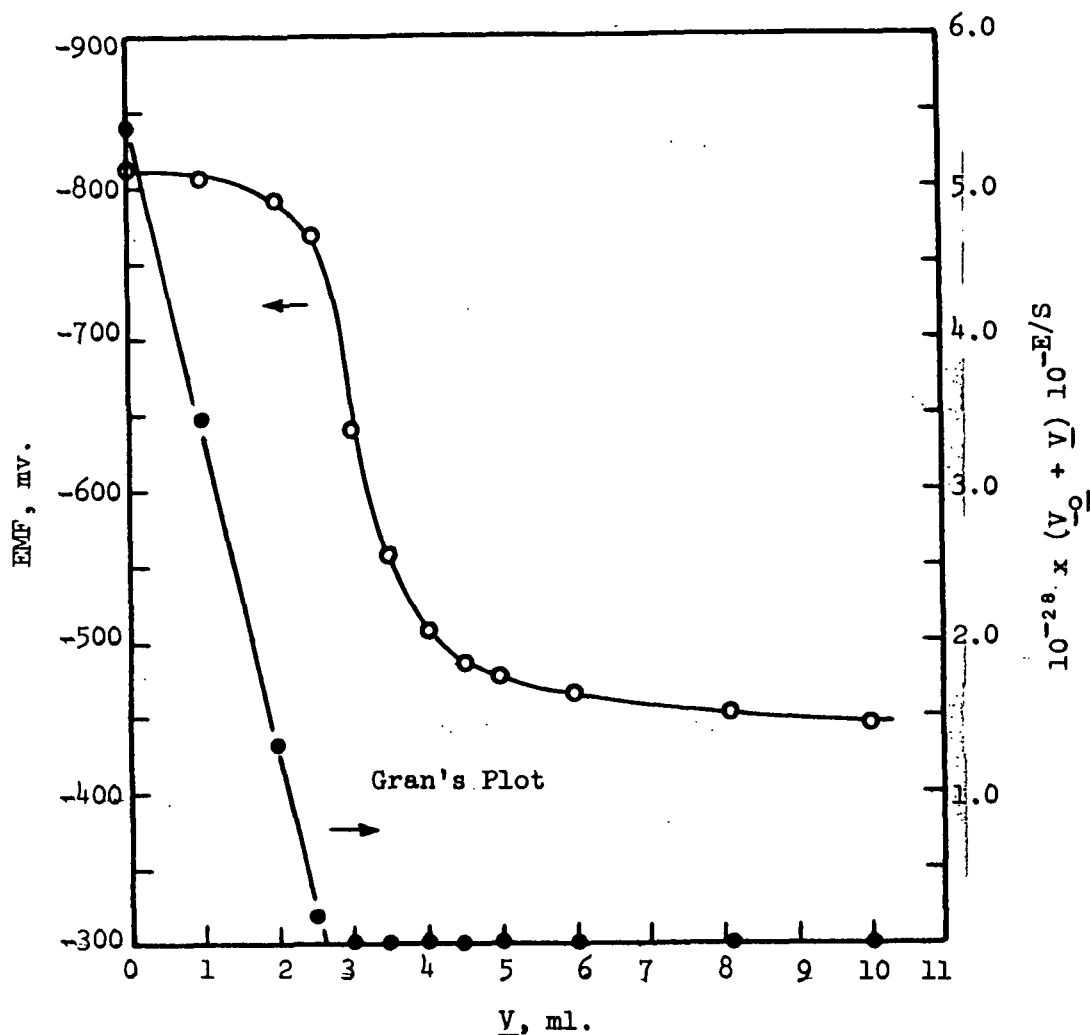


Figure 3. Potentiometric Titration: Black Liquor Sample Oxidized 60 Min., Diluted to 10% in SAOB (1:1), and Titrated With $10^{-2}M$ $Cd(NO_3)_2$. $V_0 = 50$ ml.

with appropriate $Cd(NO_3)_2$ standards. The results are listed in Table V. The Gran's plots were good at the lowest concentration even though the end point of the EMF vs. V plot was no longer discernible. Unfortunately, valid methylene blue data were not obtained for these samples because of the high pH with the NH_4Cl buffer used and discovered subsequently. The initial EMF vs. $\log C$ is linear with a slope of 26 mv. which looks promising. Its application will be discussed under direct potentiometry.

TABLE V
TITRATION DATA FROM THE OXIDATION OF BLACK LIQUOR AT 25°C.

Reaction Time, ^a min.	Initial EMF, mv.	Concn. of Titrant Cd(NO ₃) ₂ , M	V _e (Gran's end point), ml.	V _T (Apparent end point), ml.	V _O (Sample Vol.), ml.	Inorganic Sulfide Concentration in the 10% OBL Sample, M
15	-830	10 ⁻²	7.50	10.54	20	3.75 x 10 ⁻³
30	-822	10 ⁻²	5.04	8.06	30	1.68 x 10 ⁻³
45	-818	10 ⁻²	3.18	5.94	50	0.64 x 10 ⁻³
60	-811	10 ⁻²	2.60	4.00	50	0.52 x 10 ⁻³
75	-807	10 ⁻²	1.62	2.52	50	0.32 x 10 ⁻³
90	-797	10 ⁻³	8.55	11.10	50	1.71 x 10 ⁻⁴
150	-768	2 x 10 ⁻⁴	2.63	4.38	50	1.05 x 10 ⁻⁵
180	-769	2 x 10 ⁻⁴	2.50	3.45	50	1.00 x 10 ⁻⁵

^aThe oxygen flow rate was 22 ml./min. into a 200-ml. BL sample in a 800-ml. beaker.

Listed in Table VI are later data where both valid (original method) methylene blue data and good potentiometric titration data were obtained. The titration with AgNO_3 is invalid as Frant and Ross (1) state that this titrant should not be used with the SAOB solutions. The sulfide measurements directly by potentiometric titration were 1/3 to 1/5 of the values by the methylene blue sulfide measurements; thus, much of the inorganic sulfide is not directly titratable in OBL. As a point of interest, direct titration of an unoxidized black liquor sample in SAOB (1:1) with the sulfide specific electrode and Cd titrant gave the same result as a measurement by the methylene blue method.

TABLE VI
SULFIDE ANALYSES DIRECTLY BY POTENTIOMETRIC TITRATION
AND BY METHYLENE BLUE ORIGINAL METHOD

Sample	Methylene Blue	Potentiometric Titration ^a	Titration Compared with Methylene Blue, %
OBL-D plus $0.752 \times 10^{-4} \text{M}$ Na_2S	1.34×10^{-4}	0.261×10^{-4}	20
OBL-F	4.58×10^{-5}	1.62×10^{-5}	35
		1.43×10^{-5}	31
		3.60×10^{-5b}	--

^aThe OBL-D sample was done as 10% in SAOB-water 1:1 and the OBL-F sample was done as 50% in SAOB.

^bThe titrant in this sample was AgNO_3 and is therefore not valid because the titration is in SAOB (1).

An apparatus was set up to prepare, store, transfer, dilute, and titrate Na_2S in 1.0M NaOH all under a nitrogen atmosphere. Although this was successful, it was found that the SAOB system provided about the same degree of protection against

oxidation of the sulfide. The latter was used in the bulk of the work because it was simpler and more convenient. Both methods were found to be effective in protection against oxidation down to about $10^{-6}M$ sulfide. It is of interest to note that simply placing over a titration beaker a rubber sheeting (dental dam), secured with a rubber band, and fitted with holes for the electrodes, buret tip, and nitrogen gas flush line, was sufficient protection when nitrogen was flushing through the system. When the nitrogen was stopped, the electrode potential immediately began to drift in the direction of lower sulfide concentration indicating oxidation. When the nitrogen was started again, the potential would again stabilize after some minutes. At low sulfide concentrations the electrode response is probably too slow to indicate the true sulfide content during the oxidizing process.

At pH 8.5 the sulfide should be essentially in its ionized forms so no loss of H_2S can occur and $Cd(OH)_2$ is still reasonably soluble. Thus, potentiometric titrations could be made with Cd^{+2} using the sulfide specific electrode in the beginning and the cadmium specific electrode at the end, leading to measurements of both inorganic sulfide and total sulfides. A boric acid-sodium hydroxide buffer was established with a pH of about 8.5 and ascorbic acid added for antioxidant. However, both electrodes were found to be sluggish in response and produced nonlinear Gran's plots so this buffer system was dropped.

Several scrubbing solutions were tested for the possibility of absorbing the H_2S generated in the gas sweep procedure and of determining the inorganic sulfide by potentiometric titration of the contents in the trap. The results are listed in Table VII along with the methylene blue results on the same sample. It is surprising that the results from the SAOB (a buffered $2.0M$ NaOH), $2.0M$ NaOH, and $6.0M$ NaOH are all low as Thoen, DeHaas, and Austin (7) report the use of 10%

NaOH (about 6M) for removing SO₂, H₂S, and RSH in analyzing kraft gases. Even pure Na₂S is not reasonably well recovered. The buffered Cd(NO₃)₂ scrub is probably just too dilute to be affective, but the cadmium concentration cannot be increased without seriously sacrificing accuracy for the low sulfide contents expected. This discrepancy was found to be due to a recovery problem. The steps taken to give quantitative recovery will be discussed later. Prior to this, the results of (1) direct potentiometry and (2) the use of the cadmium specific electrode will be considered as part of the discussion on potentiometric methods.

TABLE VII
POTENTIOMETRIC TITRATION OF SCRUBBING SOLUTIONS

Sample	Sulfide Concentration, M		Scrub Solution	Percent Recovery
	Methylene Blue	Potentiometric Titration		
0.83 x 10 ⁻⁴ M Na ₂ S		0.46 x 10 ⁻⁴	SAOB	55
OBL-A	1.15 x 10 ⁻⁴	0.183 x 10 ⁻⁴	2.0M NaOH under N ₂	16
OBL-F	4.05 x 10 ⁻⁵	1.04 x 10 ⁻⁵	6.0M NaOH under N ₂	34
OBL-A	1.15 x 10 ^{-4a}	0.0	2 x 10 ⁻⁴ CdNO ₃ _b in Orion buffer	0

^a A sulfide concentration of 1.04 x 10⁻⁴ M was found in the Cd(OH)₂ suspension following the Cd(NO₃)₂-Orion buffer scrub.

^b From the Orion Applications Bulletin No. 15: 20 g. NaOH and 57.5 ml. of glacial acetic acid per liter.

Direct Potentiometry. Direct potentiometric measurements of sulfide concentration has great appeal because of simplicity and speed. Swartz and Light (8) investigated this application to sulfide contents of BL. The results with Na_2S solutions in SAOB (1:1) are given in Fig. 4. The slope is 33 mv. which is reasonably close to 30 mv. expected from the Nernst equation at room temperature and the duplication was found to be good. The 10^{-6}M value is suspected of being low due to oxidation and ignoring this datum would make the slope closer to 30 mv. The results with some OBL samples are listed in Table VIII along with the potentiometric titration measurements. The EMF calibration for OBL is taken from the data given in Table V. The direct potentiometric measurements are decades lower than the titration values which, in turn, are probably 1/3 to 1/5 the true value as based on the above experience. Thus, direct potentiometry does not lead even to an order-of-magnitude estimate of sulfide in OBL.

Cadmium Specific Ion Electrode

Orion has published (1,9) a method of analyzing BL using a cadmium specific electrode with an acetate buffer. Tests were made with this electrode and buffer at Na_2S concentration of 10^{-4} to 10^{-6} molar. The electrode response was erratic so the system was abandoned.

The response of the cadmium specific electrode in a boric acid buffer solution of Na_2S , discussed previously, was also found to be erratic.

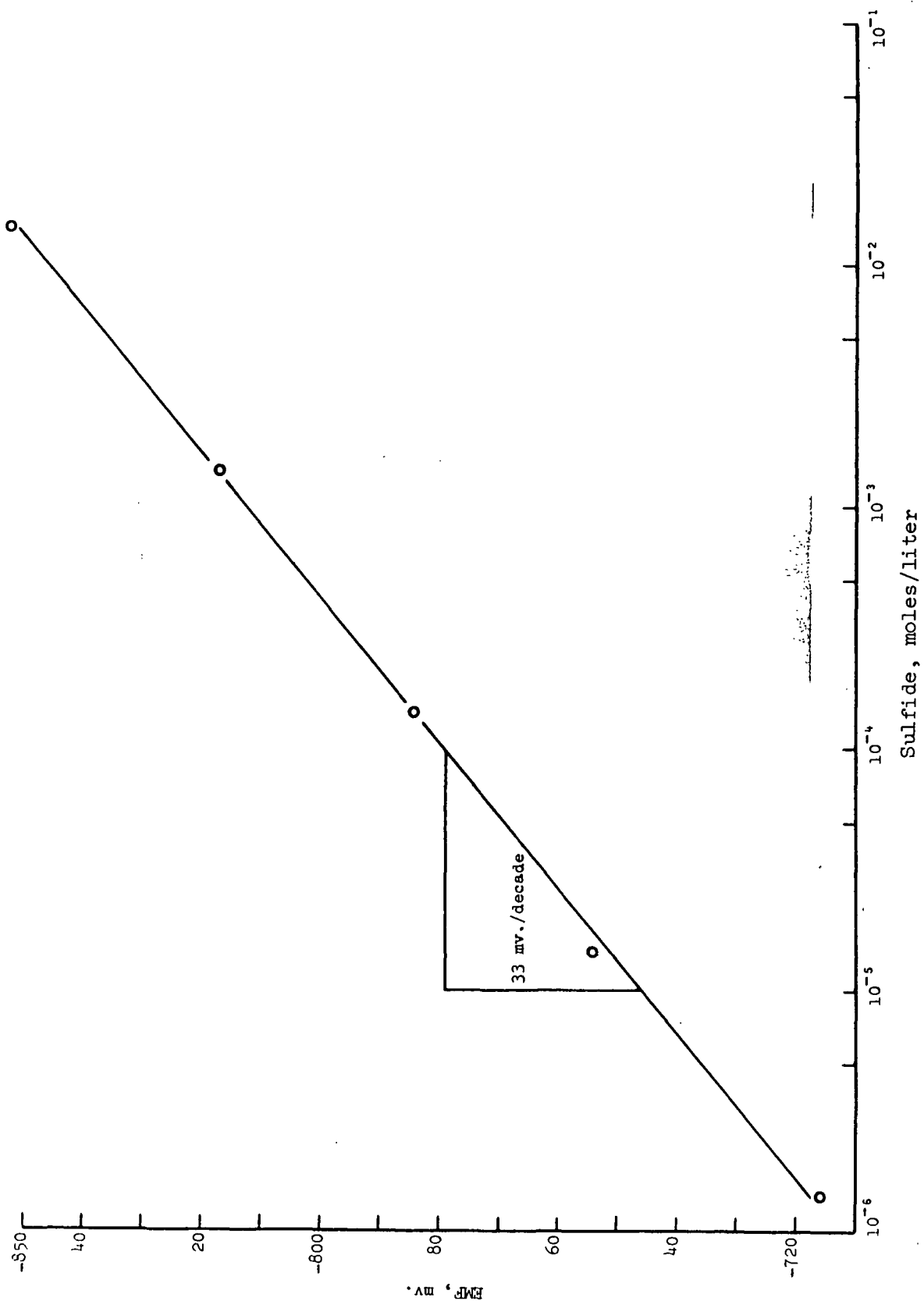


Figure 4. Direct Potentiometry of Na_2S

TABLE VIII
SULFIDE CONCENTRATIONS BASED ON INITIAL EMF
AND ON POTENTIOMETRIC TITRATION
FOR SOME OBL SAMPLES

Initial EMF, mv.	Sulfide Concentration, <u>M</u>	
	Direct Potentiometry ^b	Potentiometric Titration
-745	1.01×10^{-6}	2.61×10^{-6}
-738	6.60×10^{-7}	2.63×10^{-5}
-733	4.30×10^{-7}	1.96×10^{-5}
-682	4.30×10^{-9}	4.10×10^{-5}
-688	7.50×10^{-9}	3.57×10^{-5}
-616	1.00×10^{-11}	3.60×10^{-6a}

^aThe titrant in this case was AgNO_3 . For all others it was $\text{Cd}(\text{NO}_3)_2$.

^bBased on the initial EMF-concentration data presented in Table V.

Tuning Up the Gas Sweep System

Returning to the question of the discrepancy between titration measurement of recovered H_2S and the methylene blue measurement, samples of Na_2S in SAOB (1:1) ranging from 10^{-1}M to 10^{-4}M were titrated directly and were put through the gas sweep H_2S isolation procedure using SAOB as absorbant followed by a CdSO_4 -boric acid scrub. The results are listed in the first part of Table IX. The analysis of the original samples was quantitative showing that potentiometric titration with the sulfide specific electrode and Cd^{+2} as titrant is effective to at least a minimum concentration of 10^{-4}M sulfide. [Titrant concentrations of 10^{-3}M $\text{Cd}(\text{NO}_3)_2$ are stable indefinitely, whereas some end point trouble was encountered using 10^{-4}M $\text{Cd}(\text{NO}_3)_2$.] No sulfide was found in the CdSO_4 -boric acid scrub as measured by the methylene blue method. Thus, the low recovery in the SAOB trap was due to low release or poor carryover of H_2S in the gas sweep system.

TABLE IX
THE POTENTIOMETRIC TITRATION ANALYSIS OF Na_2S SOLUTIONS

Nominal Concentration, $\overline{\text{M}}$	Direct Titration		Release Buffer ^a		Recovered ^b Titration		Percent Recovery
	Initial EMF	Concentration, $\overline{\text{M}}$	Concentration, Vol., $\overline{\text{M}}$ ml.	Final pH	Initial EMF	Concentration, $\overline{\text{M}}$	
<u>Using the Original Gas Train System</u>							
10^{-1}	-877	0.908×10^{-1}	--	--	--	--	
10^{-2}	-842	0.908×10^{-2}	0.25	5.10	-807	0.211×10^{-2}	24.2
	-844	0.836×10^{-2}	--	--	-832	0.876×10^{-2c}	102.0
10^{-3}	-812	0.908×10^{-3}	0.25	5.10	-776	0.324×10^{-3}	35.7
10^{-4}	-780	0.929×10^{-4}	0.25	5.10	No end point using $10^{-4}\overline{\text{M}}$ CdNO_3		
<u>Using the All Glass Gas Train System with a Straight-Walled, Vertical Condenser</u>							
10^{-3}	-777	0.900×10^{-3}	$0.25 + 1 \text{ ml.}$ concd. HCl	90	-780	0.494×10^{-3}	54.9
10^{-3}	-762	0.894×10^{-3}	$0.25^d + \text{HCl}$	90	-779	0.670×10^{-3}	75.1
10^{-3}	--	0.894×10^{-3}	$0.25^d + \text{HCl}$	90	-782	0.598×10^{-3}	67.1
10^{-3}	--	0.900×10^{-3}	0.21^e	90	-786	0.832×10^{-3}	92.7
10^{-3}	--	0.894×10^{-3}	0.50	90	-776	0.794×10^{-3}	88.8
10^{-3}	-783	0.880×10^{-3}	0.50	90	-782	0.731×10^{-3}	83.2
10^{-1}	-833	0.918×10^{-1}	0.50	90	-833	0.780×10^{-1f}	82.9

^aThe acid buffer is potassium hydrogen phthalate, except as indicated. Water (when required) and 10 ml. of sample in SAOB (1:1) were added to make the total volume 100 ml.

^bThe scrubbing solution is 10 ml. of SAOB. This is transferred to a beaker using an equal volume of water where the titration is carried out.

^cThis is the indicated Na_2S sample in SAOB (1:1) placed at the end of the gas train thus being exposed to the N_2 flush for the time of the run.

^dThe order was changed so that the 1 ml. of concentrated HCl was diluted to 20 ml. with water and added after the buffer was added to the sample.

^eThe reagent used in this run was 0.2M HCl.

^fColorimetric analysis of the CdSO_4 -boric acid scrub following the SAOB scrub showed $0.8 \times 10^{-4}\text{M}$ Na_2S .

To check on this release and carryover efficiency, solutions of 10^{-4}M Na_2S were treated directly to give the methylene blue color. The absorbance of this was compared with the absorbance produced by a 10^{-3}M Na_2S put through the gas train system. The results are listed in Table X. The low recovery confirms the problems. Bubbling nitrogen from the gas train through a sample did not affect it. The original gas sweep apparatus and buffer, gave reproducible results which were calibrated on the basis of absorbance produced by known sulfide solutions as demonstrated above. However, the original apparatus did not produce quantitative transfer of H_2S .

The Apparatus

To get rid of sources of potential H_2S loss in the apparatus, it was modified in the following stages: replaced all Tygon tubing with glass (joints were made with shrinkable Teflon tubing), installed a straight-walled condenser placed in vertical position to minimize the hold up of water condensate, and, finally, replaced all rubber stoppers with glass so the system was all glass. The results are listed in Table X. Each apparatus change caused some improvement but the greatest improvement was due to the straight-walled, vertical condenser suggesting that H_2S absorption in water condensate has a significant influence on H_2S recovery.

The Release of Sulfides

With regard to release of H_2S , the final pH (5.10) of the original system buffer with sample appeared to be too high. The concentration and volume of potassium hydrogen phthalate was increased in steps and the recovery determined at each step. The results are listed also in Table X. A significant increase in recovery was achieved by 90 ml. of 0.5M with a final pH of 4.40. The higher concentration

TABLE X

THE RECOVERY OF $0.929 \times 10^{-4} \text{M}$ Na_2S BY GAS SCRUBBING USING
THE METHYLENE BLUE METHOD OF SULFIDE ANALYSIS

System	Buffer ^a			Initial Sample, ^b absorbance	Scrub Sample, ^c absorbance	Percent Recovery ^d
	Concn., M	Vol., ml.	Final pH			
Original ^f	0.25	50	--	0.670	0.115	17.2
Original with no Tygon	0.25	50	--	0.670	0.172	25.7
No Tygon, in dark	0.25	50	--	0.670	0.172	25.7
No Tygon, straight- walled condenser in vertical position	0.25	50	5.10	0.840	0.350	41.7
	0.25	90	4.70	0.670	0.450	67.3
	0.50	90	4.40	0.670	0.485	72.5
No Tygon, straight- walled condenser in vertical position with all glass	0.50	90	4.40	0.670	0.525	78.5
	1.00	90	4.40	0.670	0.530	79.2
	0.21 ^e	90	3.30	0.700	0.520	74.5

^aThe acid buffer is potassium hydrogen phthalate, except as indicated. Water (when required) and 10 ml. of sample in SAOB (1:1) were added to make the total volume 100 ml.

^bObtained by diluting $0.929 \times 10^{-1} \text{M}$ Na_2S in SAOB (1:1) to $0.929 \times 10^{-4} \text{M}$ with water, adding 10 ml. of this to 10 ml. of $\text{Cd}(\text{OH})_2$ suspension, and developing the methylene blue color in the usual way.

^cThe scrub solution was CdSO_4 -boric acid.

^dThis is based directly on the measured absorbances, so it is not an absolute value.

^eThe reagent used in this run was HCl.

^fSee the "Experimental Section" for a description.

of buffer caused some insolubility, probably of the salicylate, when the sample in SAOB (1:1) was added and no improvement in recovery was found. Likewise, the use of straight HCl to a final pH of 3.30 did not increase the recovery already achieved. It should be noted that the percentage recovery calculated is only a relative value as it is calculated from two different color systems (see footnotes b and c of Table X) for methylene blue.

A new calibration was made with the improved system and the data are listed in Table I. A comparison of calibration data shows a 1.55 increase in sensitivity over the original system. This would make the 55% recovery of Na_2S , given in Table VII, eighty-five percent by the new system. This value is confirmed by titration data discussed below.

In the event the sulfide content is so high that the color developed is too intense, the accuracy of merely diluting the color with an appropriate acid and electrolyte solution was examined. The results are listed in Table XI. The dilution leads to a value which is about 80% of the expected value when considering the lower accuracy of the absorbance values <0.1 and >1.0 .

The improved apparatus and buffer were then applied to the SAOB scrub followed by potentiometric titration. The results are listed in Table IX along with those from some other modifications of buffer. The addition of strong acid to the buffer is not as effective as increased concentration of buffer. The final recovery is about 85% even for concentrations as high as 10^{-1}M sulfide with only one SAOB trap (less than 0.1% of H_2S went through the trap at this high concentration). The 15% unaccounted for is probably held up by being absorbed in the water condensate on the walls of the condenser.

TABLE XI

THE EFFECT ON THE SULFIDE ANALYSIS OF DILUTING
THE METHYLENE BLUE COLOR DEVELOPED

Na ₂ S Concn., <u>M</u>	Absorbance ^a	Twofold Dilution, ^b absorbance	Percent Recovery
1 x 10 ⁻⁴	0.305	0.152	99.5
2 x 10 ⁻⁴	0.575	0.220	76.6
3 x 10 ⁻⁴	0.780	0.316	81.1
5 x 10 ⁻⁴	1.08	0.436	80.8
10 x 10 ⁻⁴	1.70	0.165 ^c	97.2

^aThe scrub solution in CdSO₄-boric acid.

^bThe dilution is made with a solution containing the same acid and electrolyte concentrations which are in the developed color solution, namely: CdSO₄-boric acid at 0.2% and 0.4% by weight, respectively, in 0.55M sulfuric acid 3 parts acid to 97 parts water by volume).

^cThis was a tenfold dilution.

The initial EMF values of all of these Na₂S solution titrations are listed also in Table IX. These data are plotted in Fig. 5. The set of direct titrations covering the concentration decades gave initial EMF vs. log concentration results essentially identical with the previous direct potentiometry calibration curve (Fig. 4). The recovered sample data and subsequent data testing the improved system gave initial EMF data that are self-consistent but different from the "calibration." Thus, sulfide determination by direct potentiometry measurement of the SAOB scrub would not be very accurate but it would provide an estimate of the sulfide content useful for deciding what concentration of Cd(NO₃)₂ titrant to use.

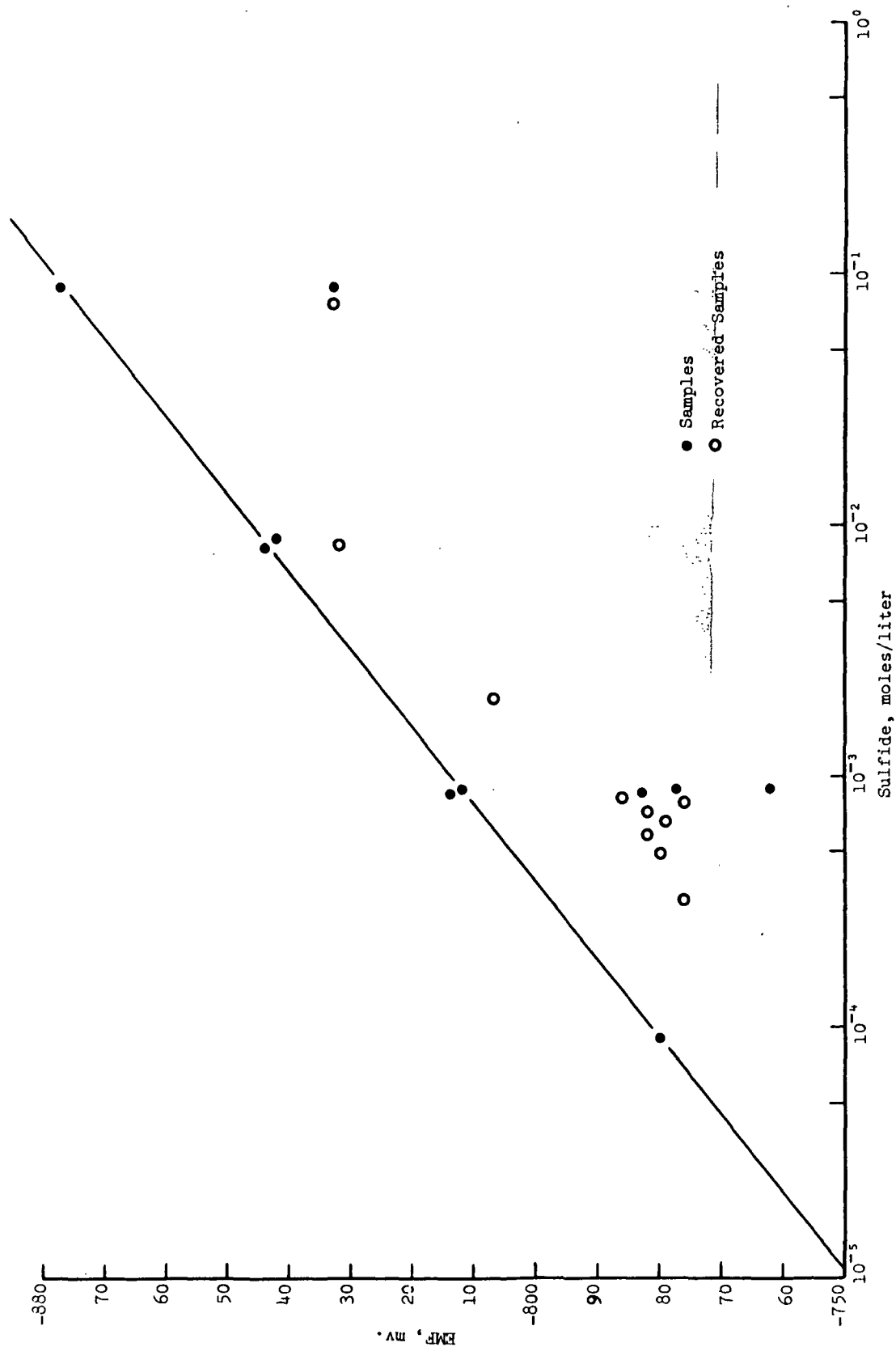


Figure 5. Direct Potentiometry of Na₂S

To summarize, OBL samples stabilized with an equal volume of SAOB may be analyzed for inorganic sulfide content by using the gas sweep method of isolating the H_2S and trapping it either in SAOB for potentiometric titration or $CdSO_4$ -boric acid for colorimetric analysis. The first method is useful for concentrations of sulfide from 10^{-1} to 10^{-4} molar, with the lower limit requiring tenfold concentration in the trapping step and $10^{-3}M$ $Cd(NO_3)_2$ titrant. The second method is useful over the concentration range $10^{-3}M$ to $10^{-6}M$ sulfide, with the lower limit again requiring a tenfold concentration and the upper limit requiring a dilution of the color to be measurable.

Analytical Skills Required and Cost

The skills required to carry out these procedures are about the same as required for the potentiometric titrations of BL. The gas sweep system can be assembled from standard laboratory glassware. For those mills already set up for potentiometric titrations, the $Ag-(Ag)_2S$ and reference electrodes would be replaced with the sulfide specific ion electrode and double junction reference electrode which represents a modest investment. The colorimetric work would require another modest investment in an absorption spectrophotometer and some cells. All of the other remaining needs such as a nitrogen supply, glassware, and reagents are obtained from standard laboratory suppliers. The analysis requires about one hour to perform. Half of this time is in the gas sweep step. It may be possible that this could be shortened by increasing the nitrogen flow rate and determining more precisely how long it takes to transport the sulfide. If the electrodes were placed directly in the SAOB scrub, potential readings during the sweep would indicate when all of the sulfide is transported and the approximate final concentration of sulfide in the scrub.

ORGANIC SULFIDES

The determination of organic sulfides, such as mercaptans, dialkyl sulfides, and dialkyl disulfides, in OBL was attempted by (1) trapping them in AgNO_3 following the Cd scrubs in the gas sweep system and, (2) trapping them in cold (-78°C. , i.e., dry ice-acetone) ethyl benzene (8) in a gas sweep system.

The results of the first method are given in Table XII. The pH of the CdSO_4 -boric acid scrub (about 8) is such that all of the organic sulfides including the mercaptans should pass through. Significant amounts of sulfide were found in both 10^{-4}M AgNO_3 traps indicating a marginal efficiency of this dilute AgNO_3 . However, the low concentration of AgNO_3 is necessary for accuracy in measuring the low levels of sulfide expected. The high pH of the $\text{Cd}(\text{OH})_2$ scrub would probably not allow the mercaptans to pass. Unfortunately, only one AgNO_3 trap was used with the $\text{Cd}(\text{OH})_2$ scrub. In either case, the organic sulfide content of OBL appears to be of the same order as the inorganic sulfide. There is a note of caution created by additional work. A spike of $0.5 \times 10^{-5}\text{M}$ dimethyl disulfide was added to OBL-E and the analysis repeated with CdSO_4 -boric acid scrub followed by two AgNO_3 scrubs. Only 1.0×10^{-5} total organic sulfide was recovered which is less than the original value of 6.0×10^{-5} . No explanation can be offered other than ineffective trapping due to the low concentration of AgNO_3 .

In using ethyl benzene at -78°C. , Cave (10) reports that the H_2S passes through while the organic sulfides remain. The results with this trap are given in Table XIII. No sulfide was found in the final CdSO_4 -boric acid trap even when the temperature of the ethyl benzene trap was held at -50°C. where the vapor pressure of H_2S should be even relatively higher (compared to -78°C.) than the organic sulfides.

Sample	Inorganic Sulfide Scrub Concn., \bar{M}	Organic Sulfide Concentration						Total, \bar{M}
		First Trap			Second Trap			
		AgNO ₃ Initial, \bar{M}	AgNO ₃ Final, \bar{M}	Diff., \bar{M}	AgNO ₃ Initial, \bar{M}	AgNO ₃ Final, \bar{M}	Diff., \bar{M}	
OBL-E	CdSO ₄ , 7.00×10^{-5}	7.70×10^{-5}	3.90×10^{-5}	3.80×10^{-5}	7.70×10^{-5}	5.50×10^{-5}	2.20×10^{-5}	6.00×10^{-5}
OBL-F	Cd(OH) ₂ , 4.05×10^{-5}	8.51×10^{-5}	7.53×10^{-5}	0.98×10^{-5}	—	—	—	0.98×10^{-5}
OBL-F	Cd(OH) ₂ , 5.10×10^{-5}	8.51×10^{-5}	8.22×10^{-5}	0.31×10^{-5}	—	—	—	0.31×10^{-5}

^a Determined by using the Ag^+ (i.e., sulfide) specific electrode and NaBr titrant.

TABLE XIII
SULFIDE DETERMINATION BY MEANS OF COLD ETHYL BENZENE
TRAPS EXTRACTED WITH AgNO_3^a

Sample	Trap Temp., °C.	Inorganic Sulfide by Methylene Blue, \bar{M}	Total Sulfide Concentrate, \bar{M}							Organic Sulfide, \bar{M}
			First Trap			Second Trap				
			AgNO_3 Initial	AgNO_3 Final	Diff.	AgNO_3 Initial	AgNO_3 Final	Diff.	Total	
OBL-F	-78	4.58×10^{-5}	8.25×10^{-5}	7.80×10^{-5}	0.45×10^{-5}	8.25×10^{-5}	5.34×10^{-5}	2.91×10^{-5}	3.36×10^{-5}	0.84×10^{-5}
OBL-F	-50	4.58×10^{-5}	8.25×10^{-5}	4.63×10^{-5}	3.62×10^{-5}	8.25×10^{-5}	7.90×10^{-5}	0.35×10^{-5}	3.97×10^{-5}	1.45×10^{-5}

^a Determined by potentiometric titration using Ag^+ (i.e., sulfide) specific electrode and NaBr as titrant.

^b No methylene blue color developed in the $\text{Cd}(\text{OH})_2$ suspension trap following the cold ethyl benzene.

^c Assumes that the true H_2S concentration released by this original gas train system is 55% of the indicated methylene blue-analysis sulfide.

Therefore, all of the sulfides stayed in the cold ethyl benzene. Because the quantities of H_2S involved with the present samples are considerably less than in Cave's samples (e.g., 0.02 mg. H_2S in this work compared with Cave's 32 mg. or 6.41 mg. which he reports left 1.0 mg. and 0.48 mg., respectively, in the cold ethyl benzene), perhaps the solubility limit of H_2S in cold ethyl benzene was never reached here. It is interesting to note that if the amount of H_2S is subtracted from the total (assuming 55% true recovery of H_2S based on the methylene blue value), the amount of organic sulfides so calculated is about equal to that determined above by the $AgNO_3$ trap. If these results are valid, then the organic sulfides of OBL-F did not contain much mercaptans since they are excluded in the $Cd(OH)_2$ scrubbed samples. This is reasonable since, under oxidizing conditions, mercaptans are transformed into disulfides (11). These data also suggest that the extraction of the ethyl benzene solution with dilute $AgNO_3$ was reasonably effective.

Although no method of determining organic sulfides in OBL is clearly established, some promising leads are suggested. Each of these approaches starts with the gas sweep isolation of the sulfides. One possibility is to put the sulfide gases through selective scrubbers or absorbers and allow the remaining sulfides to be oxidized by Br_2 whose concentration is determined by titration in coulometric cells similar to Barton titrators as described, for example, by Thoen, et al. (7) or Adams, et al. (12). The other possibility is to condense the sulfide gases into a cell, the contents of which can be subsequently introduced directly into a gas chromatograph. Such a method would be very sensitive as the condensing is self-concentrating, very specific to identifiable sulfides, simultaneously quantitative for each sulfide, and rapid.

CONCLUSIONS

With the OBL samples handled conveniently in SAOB, their inorganic sulfide content may be determined quantitatively over the concentration range 10^{-1} to 10^{-6} M sulfide. The first three decades of concentrations require potentiometric titrations of the isolated H_2S , using the sulfide specific ion electrode and $Cd(NO_3)_2$ as titrant. The last three decades require colorimetric measurements of the methylene blue developed from the isolated sulfide.

The potentiometric titration of OBL directly in SAOB can be done using the sulfide specific ion electrode and $Cd(NO_3)_2$ as titrant but the value is 1/3 to 1/5 the methylene blue value. Direct potentiometry in this system is not valid, although when applied to the isolated H_2S system it can be used as a rough approximation of the true value.

It may be possible to determine the organic sulfides both as to kind and amount by use of the sulfide isolation procedure coupled to a coulometric titration or a gas chromatograph.

EXPERIMENTAL PROCEDURES

PREPARATION OF BUFFERS AND REAGENTS

All chemicals used are reagent-grade quality.

Sulfide Antioxidant Buffer, SAOB, (1)

Add 40.0 g. of NaOH to a 500 ml. volumetric flask. Put about 250 ml. of distilled water into the flask, dissolve the alkali and cool the contents to room temperature. Next, add 160.0 g. of sodium salicylate to the cooled flask, dissolve the buffer, and cool if necessary. The solution will be straw colored. Finally, add 36.0 g. of ascorbic acid to the flask and dissolve the antioxidant. Dilute to the mark with distilled water. The final solution, light brown in color, must be stored in a tightly stoppered bottle, e.g., ground glass stopper with Parafilm seal wrapped around the cap. It is normal for a brown ring and crust to form on the surface of the stored contents. However, discard when the solution develops heavy sediment and turns dark.

Sodium Sulfide Standard, $10^{-4}M$

Place a quantity of $Na_2S \cdot 9H_2O$ crystals on some filter paper, wash them with distilled water, and dry them with filter paper. This will remove the oxidized surface material. Add 2.40 g. of these dry crystals to a 100-ml. volumetric flask, pipet in 50.0 ml. of SAOB, dissolve the crystals, fill to the mark with distilled water and mix. Keep flask tightly stoppered. Determine the sulfide concentration by potentiometric titration of an aliquot using the sulfide specific ion electrode with the double junction reference electrode and standard $Cd(NO_3)_2$ as titrant.

Cadmium Hydroxide Suspension, (3)

Add 4.3 g. of $3N$ $CdSO_4 \cdot 8H_2O$ to a one-liter volumetric flask, along with 0.3 g. of $NaOH$, add distilled water, dissolve, and fill to the mark. Mix the suspension well each time before using.

Amine Solution, (3)

Prepare the amine-acid stock solution by adding 50 ml. of concentrated sulfuric acid to 30 ml. of distilled water and cool. Add 12.0 g. of N,N -dimethyl- p -phenylenediamine (or 16.3 g. of its sulfate) and stir until dissolved. Store this solution in a refrigerator where it will keep almost indefinitely.

Prepare the amine-sulfuric acid test solution by diluting 25 ml. of the stock solution to one liter with 1 to 1 sulfuric acid. This test solution will keep under refrigeration for up to about one month.

Ferric-Chloride Solution, (3)

Dissolve 100 g. of $FeCl_3$ in distilled water and dilute to 100 ml.

Cadmium Nitrate Standard, $10^{-1}M$

Dissolve 30.8 g. of $Cd(NO_3)_2 \cdot 4H_2O$ in distilled water in a one-liter volumetric flask and dilute to the mark. Standardize this by titrating an aliquot with a standard EDTA solution (37.22 g. of disodium ethylenediamine tetraacetate per liter solution is 0.1 normal) using Eriochrome black T as indicator.

Cadmium Sulfate-Boric Acid Scrub, (7)

Dissolve 37 g. of $3N$ $CdSO_4 \cdot 8H_2O$ and 20 g. of boric acid (H_3BO_3) in distilled water in a one-liter volumetric flask and dilute to the mark.

Silver Nitrate Standard, $10^{-1}M$

Dissolve 17.0 g. of $AgNO_3$ in distilled water in a one-liter volumetric flask and dilute to the mark. Keep this solution in the dark. Titrate an aliquot of this potentiometrically with a standard NaBr solution using the silver specific (i.e., the sulfide specific) ion electrode and the double junction reference electrode.

Solutions of $AgNO_3$ with concentration lower than about 10^{-3} should be handled in the dark and in polypropylene containers to minimize the effect of photo-decomposition and adsorption on the results.

ELECTRODES

Sulfide Specific Ion Electrode

The Orion (Cambridge, Mass.) Model 94-16A sulfide and silver specific ion electrode was used in this study. The instruction manual accompanying this electrode is rather complete and should be followed. Treating the surface of the electrode body and sensing element with the silicon oil provided, as per instructions and wiping the surface occasionally with cellosolve will keep the electrode clean and free of black liquor residue.

The only interference reported is with mercury, whose sulfide is more insoluble than silver sulfide. It is, therefore, essential that the Orion double junction reference electrode be used. Do not use fiber- or frit-type reference electrodes as the chloride in these electrodes will form silver chloride at the junction, resulting in drifting readings.

Our experience has been that the electrode response time varies from something less than a minute to five or ten minutes with a stirred sample. This depends primarily on the sulfide concentration, the lower the concentration the longer the time. Thus, the longest response time is at or near the equivalence point. With unstirred samples, the response time approaches fifteen minutes to one hour.

Occasionally erratic or drifting response was experienced. Very often this behavior was a direct function of the stirring speed. The electrode should not be used until this problem is overcome. Usually the trouble was in the double junction reference electrode discussed below. Cleaning the electrode with solvent and a soft tissue, and possibly shaking it gently like one would a fever thermometer, would help.

Double Junction Reference Electrode

The sleeve-type double junction reference electrode must be used with the sulfide specific electrode. The Orion, Model 90-02 was employed. The instruction sheet accompanying the electrode is quite complete and should be followed. As per instructions, the inner chamber solution was changed once a week and the outer chamber solution every day. Since the SAOB diluted 1:1 is 1.0M NaOH, the outer solution was 10% by weight KNO₃ in 1.0M NaOH to make the pH compatible with the sample, as instructed. In the refilling process the outer sleeve must be pulled back from the electrode tip, as instructed. We found that in reseating the sleeve, it does not have to be flush with the tip, as instructed, but needs to be just snug enough to prevent leakage. A sleeve was cracked in attempting to force it flush with the tip.

Erratic and drifting electrode response was very often due to the double junction reference electrode. This was usually solved by refilling the outer chamber solution or both the inner and outer solutions, making sure there were no air bubbles trapped. It is felt that the problem was probably the hangup of a microscopic bubble, particularly at the pinhole connecting the inner and outer chamber.

Cadmium Specific Ion Electrode

The Orion, Model 94-48A, cadmium specific ion electrode, was used, as per the instruction manual accompanying the electrode. The double junction reference electrode was employed with it. The performance with standard $\text{Cd}(\text{NO}_3)_2$ solutions in neutral to acid solutions was as described by the manufacturer. However, erratic and drifting response was experienced in an attempt to operate with sulfide in a boric acid buffer at pH 8.5 and in the Orion acetate buffer at cadmium concentrations of 10^{-4} molar or under.

POTENTIOMETRIC MEASUREMENTS

A Heathkit (Benton Harbor, Mich.) Model EUW-20A recording potentiometer with a pH module, Model EUA 20-11, was used to measure the EMF of the electrodes. This recorder had been converted to the Heathkit Zener diode reference voltage source which was found to have very good long term stability. The potentiometer was calibrated every few weeks with an accurately known voltage source and very little drift was observed. The only shortcoming of this inexpensive recording potentiometer is a tendency of the string drive of the pen to bind.

In making the EMF measurements, both electrodes were rinsed with distilled water and wiped dry with clean soft tissue. The tips of the electrodes were immersed in the sample such that there was no interference with the magnetic stirrer. The sample was stirred magnetically with a Teflon coated bar. A sponge or other insulator must be placed between the magnetic stirring plate and the sample container so that the sample does not heat up from the stirring motor.

In potentiometric titration after each titrant addition you must be sure that the electrodes have reached EMF equilibrium before adding the next increment of titrant. The recording feature of the potentiometer used was convenient for this purpose.

All of the computer outputs of the potentiometric titration data are filed in the Central Records of The Institute of Paper Chemistry with a copy of this report.

SULFIDE ISOLATION BY GAS SWEEP

Volatile sulfides may be released from a sample without release of SO_2 by acidifying to pH 4 (4). The procedure for doing this is described in the section "Recommended Procedure."

The original apparatus and procedure used in acquiring much of the colorimetric data in this study was the same as above with the following exceptions:

- (1) The apparatus employed Tygon tubing connections, rubber stopper fittings, and a condenser with bulblike-shaped inner surface (i.e., Allihn condenser). The latter extended from the sample flask at about 45° from the vertical position.

- (2) The acidifying buffer was 50 ml. of 0.25M potassium hydrogen phthalate plus 40 ml. of water. This was added to the 10 ml. of sample previously placed in the flask which had been flushed with nitrogen as in the "Recommended Procedure."

It should be noted that the nitrogen flow must be turned off when the acid buffer is to be added to the flask. In the early work, an empty trap was placed at the beginning of the gas scrub train. However, no fluid carryover from either direction was ever experienced and so this was eliminated.

ANALYSIS OF THE SCRUBBING SOLUTIONS

Colorimetric Procedure

The methylene blue method of determining sulfide is based on the work of Bamesberger and Adams (3). The procedure is given in the section entitled "Recommended Procedure." The spectrophotometer used was a Beckman Model DU.

In all the colorimetric experiments in this study, two traps of the scrubbing solution were placed in series, unless stated otherwise. No sulfide was ever detected in the second trap. In a similar manner, a $\text{Cd}(\text{OH})_2$ suspension or CdSO_4 -boric acid trap was placed in series following the traps used in the potentiometric work. Again no sulfide was detected except as indicated.

The colorimetric method is sensitive to the following points which should be carefully observed:

- (1) Wash all bubbling tube capillaries, both in the round-bottom flask and in the scrubbing tube, between successive runs. It is good

practice to keep the capillaries dipped into a beaker of water between runs.

- (2) Shut off the nitrogen supply while adding the potassium hydrogen phthalate buffer.
- (3) The amine acid solution (3 ml.) should be added in such a way so as to dissolve any precipitate on the capillary.

Potentiometric Titration Procedure

The procedure for the potentiometric titration of the scrubbing solution is given in the section "Recommended Procedures." The first two points above are also applicable here. It is important to note that after using 10 ml. of SAOB as scrubbing solution and using 10 ml. of water to aid in the transfer to the titration beaker, any further dilution must be with SAOB diluted 1:1 since this is the desired solvent.

OXIDATION OF BLACK LIQUOR

A 200-ml. volume of BL was placed in a one-liter beaker. A fritted glass gas diffuser tube was positioned in the center of the beaker so that it almost touched the bottom. Oxygen was metered in through a flowmeter at the rate of 20 ml./min. A second tube was positioned about one-half inch over the surface of the sample. This tube was connected to a water aspirator; thus, excess foam was removed.

The extent of oxidation was dependent on the time of sparging. This oxidation could be speeded up by heating the sample.

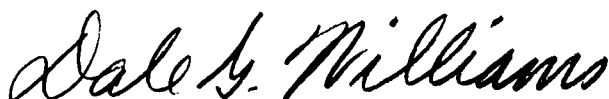
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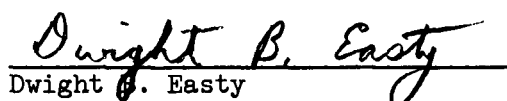
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